

**NTO-Based Explosive
Formulations: A Technology
Review**

Matthew W. Smith and
Matthew D. Cliff

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NTO-Based Explosive Formulations: A Technology Review

Matthew W. Smith and Matthew D. Cliff

**Weapons Systems Division
Aeronautical and Maritime Research Laboratory**

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ABSTRACT

3-Nitro-1,2,4-triazol-5-one (NTO) is an explosive ingredient under investigation as a potential insensitive replacement for RDX in explosive formulations. Although its performance is slightly less than that of RDX, NTO is thermally more stable and less sensitive to hazard stimuli. Explosive compositions based on NTO are therefore more likely to be Extremely Insensitive Detonating Substances, and munitions filled with them may meet the criteria of both Insensitive Munitions (IM) and HD 1.6 classification for storage and transportation. This report examines the currently available literature on NTO and its use in explosive compositions, and recommends future work to explore the possible application of NTO in IM compliant explosives for the ADF.

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NTO-Based Explosive Formulations

Executive Summary

Energetic materials are inherently hazardous, and accidents involving explosive-filled munitions have come at a high cost in terms of weapons platforms, personnel and materiel. In response to such accidents, programs have been established world wide to develop Insensitive Munitions (IM) which respond less violently to accidental environmental stimuli, and policies have been instituted to adopt such weapons into service. In line with this philosophy the ADF also has established a policy for the adoption of IM into its inventory.

There are several different approaches to the development of insensitive munitions, but prominent among them is the use of explosive fillings with reduced sensitivity, but in which performance is not compromised. Two avenues by which to approach IM-compliant explosive compositions are the substitution of sensitive ingredients with intrinsically less sensitive materials, and the use of a tough, rubbery polymeric matrix to absorb environmental "abuse" and to provide physical and chemical isolation of the energetic components.

NTO (3-nitro-1,2,4-triazol-5-one) is an insensitive but relatively powerful explosive which shows promise for application in either approach to IM-compliant formulations. In particular melt-cast based compositions may provide viable IM-compliant options for the RAAF Mk 80-series bomb fills which can be filled using Australian industry's established melt-cast TNT-based filling technology. This report reviews available literature describing the properties of NTO and its application in both melt cast TNT-based and cast-cured polymer bonded explosives, and makes recommendations regarding research and development proposed to address future requirements of the ADF for IM-compliant explosive fillings.

Authors

Matthew W. Smith

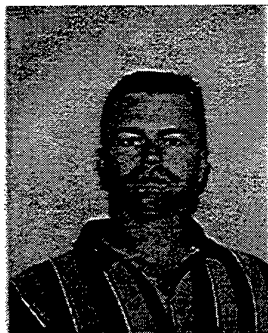
Weapons Systems Division



Matthew Smith has completed his Honours degree at the University of Adelaide in 1996 in Organic Chemistry. Following several months research work on new organometallic compounds, he commenced work at AMRL in 1997. He has worked on a range of tasks including the synthesis and thermal analysis of new energetic materials and PBX formulations. He is currently carrying out research into novel energetic materials and their uses in new insensitive formulations.

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Abbreviations

AN	-	Ammonium Nitrate
AP	-	Ammonium Perchlorate
BDNPA/F	-	Bis-(2,2-dinitropropyl) acetal/formal
CE	-	Capillary Electrophoresis
CRT	-	Chemical Reactivity Test
DKIE	-	Deuterium Kinetic Isotope Effect
DMF	-	<i>N,N</i> -Dimethyl Formamide
DMSO	-	Dimethyl Sulfoxide
DSC	-	Differential Scanning Calorimetry
DTA	-	Differential Thermal Analysis
EIDS	-	Extremely Insensitive Detonating Substance
GAP	-	Glycidyl Azide Polymer
HD	-	Hazard Division
HPLC	-	High Performance Liquid Chromatography
HTPB	-	Hydroxy Terminated Polybutadiene
IPDI	-	Isophorone Diisocyanate
IM	-	Insensitive Munitions
IR	-	Infrared
MeOH	-	Methanol
MS	-	Mass Spectrometry
NG	-	Nitroguanidine
NMP	-	1-Methyl-2-pyrrolidinone
NMR	-	Nuclear Magnetic Resonance
PBX	-	Polymer Bonded Explosive
PGA	-	Polypropylene Glycol
ppm	-	parts per million
SEM	-	Scanning Electron Microscopy
TFA	-	Trifluoroacetic Acid
TGA	-	Thermal Gravimetric Analysis
THF	-	Tetrahydrofuran
TMD	-	Theoretical maximum density
UV	-	Ultraviolet
VoD	-	Velocity of Detonation
XRD	-	X-Ray Diffraction

1. Introduction

Defence forces around the world are adopting Insensitive Munitions (IM), to minimise the response of ordnance items to accidental stimuli, thus increasing the survivability of personnel and scarce resources (both weapon systems and platforms) [1]. The application of IM can also have an important economic and logistic impact on stockpiling, storage and transport. The Australian policy is described in DI(G) LOG 07-10, which states that IM stores will be introduced where it is practical, sensible and cost effective to do so [2].

Insensitive munitions are those which reliably fulfil their performance, readiness and operational requirements on demand, but in which the violence of response to unplanned hazardous stimuli is restricted to an acceptable level [2]. There are two general approaches to explosive formulations which satisfy IM requirements [3]. The first is through the use of polymer bonded explosives (PBXs), in which the energetic (and sensitive) component is dispersed in a rubbery matrix. The second is through the use of intrinsically insensitive energetic ingredients such as 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), which is stabilised by extensive intramolecular and intermolecular hydrogen bonding.

Another possible intrinsically insensitive energetic material is 3-nitro-1,2,4-triazol-5-one (NTO). NTO is known by several synonyms such as 5-oxy-3-nitro-1,2,4-triazole (ONTA) and 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one, and has the structure shown below (1) (Figure 1). Manchot and Noll first prepared NTO in 1905 by nitration of 1,2,4-triazol-5-one (TO), although the structural assignment was incorrect [4]. Major interest in the explosive characteristics of NTO, however, developed in the mid 1980s [3].

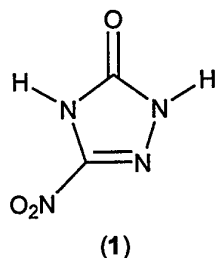


Figure 1 Structure of NTO.

NTO has improved performance over that of TATB and is much less sensitive to hazard stimuli than cyclotrimethylene trinitramine (RDX), commonly used benchmarks for insensitive and energetic properties respectively [5, 6]. Discussion in this review will be restricted to the synthesis and physical and chemical properties of NTO (and selected derivatives), and to its use in explosive and propellant formulations.

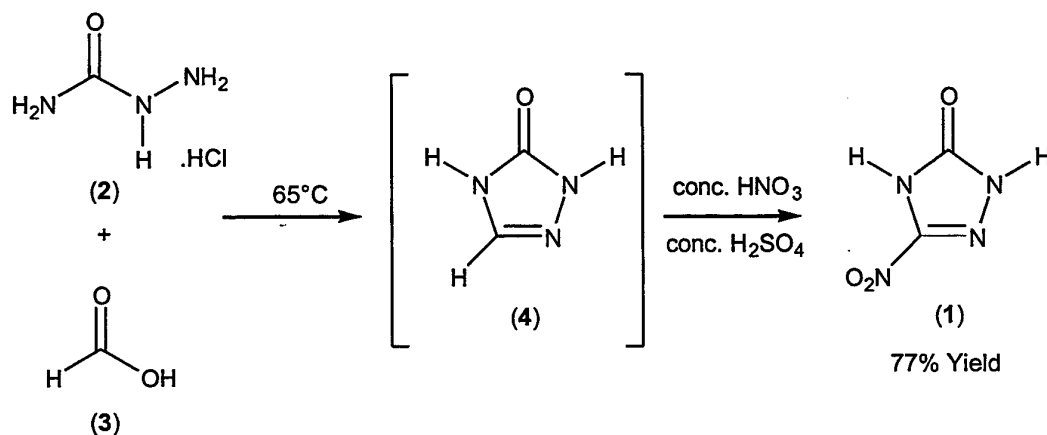
2. Properties of NTO

2.1 Synthesis

The current synthetic strategy for NTO has been altered only slightly from that reported by Russian workers in the late 1960's [7], despite considerable synthetic effort [3, 8-16]. The synthetic pathway involves two simple reactions using inexpensive starting materials and gives NTO in high yield. The two reactions can be combined in a one-pot procedure, thereby eliminating the need to isolate the intermediate triazolone (TO).

The method adopted by Australian workers closely mirrored this route and involved the reaction of semicarbazide hydrochloride (2) with formic acid (3) followed by a mixed acid nitration, in a one-pot reaction (Scheme 1) [3]. Formic acid (88%, 34.5 mL, 0.8 mol) was added to solid semicarbazide hydrochloride (33.45 g, 0.3 mol) at ambient temperature and the resulting solution was then heated to 65°C and stirred to give the intermediate 4. A mixture of neat nitric (100 mL) and 98% sulfuric acid (20 mL) was then added and the temperature maintained at 65°C for between 1.5 and 2 hours. The mixture was then cooled and filtered, and the resulting solid washed with cold water. Recrystallisation from hot water gave the target NTO (1) as a white crystalline solid in 77% yield. Other synthetic conditions varying the nitration method and reaction temperature were examined, but this route gave optimum yields and could easily be applied to larger scale reactions.

Scheme 1 Aeronautical and Maritime Research Laboratory Synthesis of NTO.



2.2 Characterisation of NTO

2.2.1 Physical and Spectral Properties

The chemical and physical properties of NTO have been extensively characterised (Table 1) [3, 5-12, 17-29].

Table 1 Chemical Properties of NTO.

Empirical Formula	C ₂ H ₂ N ₄ O ₃
Molecular Weight (g/mol)	130
Melting Point (°C)	273 (decomposition) [3]
Oxygen Balance (%)	-24.60 [26]
Crystal Density (g/cm ³)	1.911 [12], 1.93 [9-11]
Acidity (pKa)	3.76 [8], 2.35 in a 0.1 M solution [7]
NMR Spectrum (ppm) ¹ H NMR	13.5 (H-N adjacent NO ₂) and 12.8 (<i>d</i> ₆ -DMSO) [27]
¹³ C NMR	154.4 (C=O) and 148.0 (C-NO ₂) (<i>d</i> ₆ -DMSO) [8-11]
¹⁵ N NMR	-34.5 (N-H), -112.9 (N-H), -205.4, -207.4 and -243.9 [29]
IR Spectrum (cm ⁻¹)	3212 (NH), 1714 (C=O), and 1547 (NO ₂) [12]
Near IR Spectrum (cm ⁻¹)	6250 and 4550 [23]
Raman IR Spectrum (cm ⁻¹)	1361 and 1329 [28]
UV Spectrum	A _{max} @ 315nm, ε=4830 mol ⁻¹ .cm ⁻¹ [8]

Ab initio calculations for the theoretical IR spectrum of NTO have shown good correlation with the experimental results, where large blue shifts of up to 100 cm⁻¹ were seen due to the extensive hydrogen bonding between the NH groups and the carbonyl and nitro groups [21].

2.2.2 Solubility and Crystallisation Studies

NTO is soluble in water, acetone, acetonitrile, dioxan, NMP, DMF, trifluoroacetic acid and DMSO, has limited solubility in ethyl acetate, diethyl ether, chloroform and toluene, and is insoluble in dichloromethane (Table 2) [3, 8].

Table 2 Solubility of NTO in Representative Solvents.

Solvent	Temperature (°C)	Solubility (g/100 mL solvent)
Water	4.85	0.72
	18.95	1.28
	43.3	2.6
	100	~10
Acetone	18.95	1.68
Ethyl Acetate	18.95	0.28
Dichloromethane	18.95	<0.02

NTO recrystallises from water as large, jagged, rod-like crystals, which tend to agglomerate. This creates problems with explosive formulations where adverse crystal shape and size can cause handling difficulties and formulations may become highly

viscous and difficult to pour. Crash precipitation from DMSO, however, gives more appropriate crystal shapes. Dissolution of NTO in hot DMSO and subsequent injection through an opening smaller than 0.70 mm into dichloromethane produces NTO as finely divided particles with surface areas of the order of $5.7 \text{ m}^2/\text{cm}^3$ [30].

Spheroidal NTO can be formed by recrystallising crude NTO from low molecular weight alcohols such as methanol and ethanol [31]. The technique involved dissolving NTO in an alcohol of 1 to 5 carbon atoms at a temperature between 40°C and slightly below the boiling point of the alcohol used. Cooling at between 6 and 20°C per minute to a final temperature of $+5$ to -10°C while agitating the solution produced spheroidal crystals.

2.2.3 Crystal Polymorphs

NTO has been found to exist as two polymorphs [32]. The most common and more stable polymorph is α -NTO, grown by the slow cooling of a hot solution of NTO in various solvents (such as water), followed by refrigeration. The crystals appear as long needles, which shatter when cut perpendicular to the crystal axis, although they may be bent sharply without breaking, a property unusual for small organic molecules.

β -NTO is formed by recrystallisation from methanol or a mixed ethanol/dichloromethane solvent system, but decomposes within six months of formation (one source claimed that it reverted to the alpha form) [32]. Crystals of the β -polymorph for structure determination have also been obtained by cooling a hot aqueous solution of NTO, but large enough quantities for sensitivity testing have not been obtained.

Several analytical techniques have been developed to distinguish the two polymorphs, in response to safety concerns for the less stable β -form. IR spectra over the range 500 to 1800 cm^{-1} differed for the two forms (see Ref. [32] for both IR spectra), while XRD generated different diffraction patterns and crystal lattice parameters (Table 3). Scanning electron microscopy (SEM) revealed differences in the habit of the multi-crystal agglomerates.

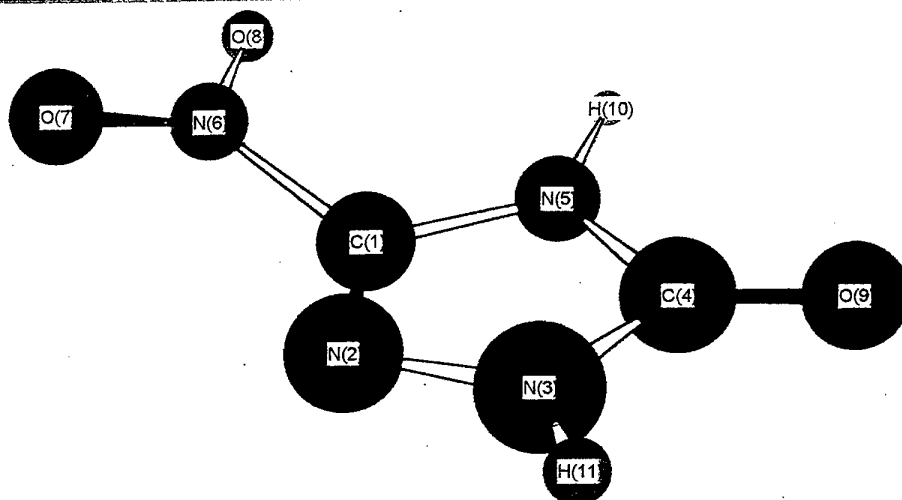
Table 3 Lattice Parameters of the α and β Polymorphs of NTO.

Crystal Polymorph	α	β
Space Group	P1	P2 ₁ /c
Unit Cell	Triclinic, 8 Molecules/Cell	Monoclinic, 4 Molecules/Cell
a (Å)	5.12	9.326
b (Å)	10.30	5.515
c (Å)	17.9	9.107
α (°)	106.7	
β (°)	97.7	100.77
γ (°)	90.2	
Density (g/cm ³)	1.92	1.878

2.2.4 X-Ray Analysis

X-ray crystallography and *ab initio* studies have provided information on the bond angles and bond lengths of NTO. Table 4 lists bond angles and lengths determined by quantum mechanical calculations [33], which have been used to provide the 3-dimensional NTO structure generated from the Chem 3D program [34], and which correspond well with experimental results [32].

Table 4 Optimised Bond Lengths (Å) and Angles (°) of NTO [33].



Bond Lengths					
C(1)-N(2)	1.266	C(1)-N(5)	1.364	C(1)-N(6)	1.419
N(2)-N(3)	1.400	N(3)-C(4)	1.385	N(3)-H(11)	0.994
C(4)-N(5)	1.392	C(4)-O(9)	1.204	N(5)-H(10)	0.996
N(6)-O(7)	1.230	N(6)-O(8)	1.251		
Bond Angles					
N(2)-C(1)-N(5)	114.3	N(2)-C(1)-N(6)	124.9	N(5)-C(1)-N(6)	120.8
C(1)-N(2)-N(3)	103.2	N(2)-N(3)-C(4)	112.9	N(2)-N(3)-H(11)	119.8
C(4)-N(3)-H(11)	127.3	N(3)-C(4)-N(5)	101.6	N(3)-C(4)-O(9)	129.1
N(5)-C(4)-O(9)	129.3	C(1)-N(5)-C(4)	108.0	C(1)-N(5)-H(10)	125.4
C(4)-N(5)-H(10)	126.6	C(1)-N(6)-O(7)	118.1	C(1)-N(6)-O(8)	114.5
O(7)-N(6)-O(8)	127.4				

Information related to the crystal packing, unit cell dimensions, powder diffraction pattern and molecular dynamics has also been reported [21, 22, 25, 32].

2.2.5 Computational Studies

Ab initio molecular orbital studies indicated the most stable tautomers of NTO and its conjugate base to be (I) and (II) respectively (Figure 2), as predicted intuitively from

stabilisation effects of the electron withdrawing ketone and nitro groups [19, 21, 24, 33].

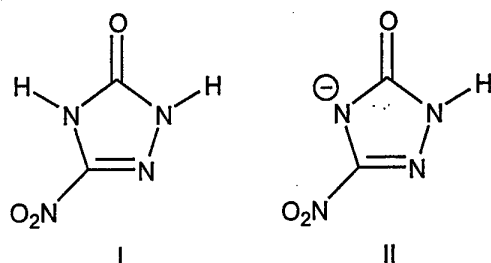


Figure 2 Thermodynamically most Stable Forms of NTO and its Conjugate Base

2.2.6 Chromatographic Studies

Chromatographic procedures for separating NTO from the starting triazolone (TO) [35], related cyclic amines [18], and other energetics (cyclotetramethylene tetranitramine (HMX), RDX, tetryl, pentaerythritol tetranitrate (PETN) and trinitrotoluene (TNT) and related aromatics) [17, 35] have been developed by numerous workers. High performance liquid chromatography (HPLC) and capillary electrophoresis (CE) techniques were able to separate different mixtures, generally within a fifteen minute elution period (Table 5), although retention times of as long as 40 minutes have been seen [18]. French workers have successfully used HPLC and CE methods to detect NTO in pre-prepared soil samples, leading to techniques that could possibly be applied to detection of NTO and the monitoring of its biological degradation in the environment [18].

Table 5 Successful HPLC Methods.

	NTO/TO [35]	Explosive Mixture [35]	Amine Mixture [18]
Solvent Flow	Isocratic	Isocratic	Gradient
Solvents	MeOH 18%, THF 2%, TFA 80% (Buffer pH 6.7)	MeOH 45%, THF 5%, H ₂ O 50% (Buffer pH 2)	TFA, Acetonitrile, TFA
Flow Rate (mL/min)	1	1.5	1
Column	Waters rad.pack 080100	Supleco 5-8220	Hypercarb
Packing Name	Novapack C18	Suplecosil 1c18	Porous Graphitic Carbon
Packing Material	4	5	7
Particle Size (µm)			
Detector Wavelength (nm)	220	220	220

2.2.7 Commercial Sources

Four classes of NTO are produced at the SNPE plant in France, with varying mean particle size [36]. Sieving of recrystallised NTO gives classes I and II, with mean particle sizes of 450 µm and 320 µm respectively. Classes III and IV are obtained by

grinding and sieving the class I and II material. The mean particle size for class III is 68 μm , and for class IV is 17 μm . Production is expected to increase to 25 000 kg per annum [37].

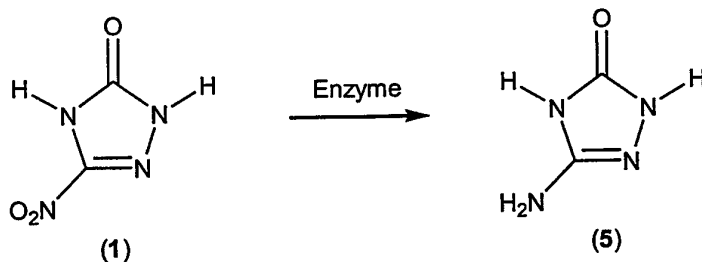
A US review in 1990 reported only one facility for production of NTO in the USA, with the manufacturing scale insufficient to meet requirements even of an experimental program filling Mk 82 and 84 bombs with the NTO based PBX, PBXW-122 [38]. A consortium of Olin and Ensign-Bickford had the capability of producing half a million kilograms per year, but were looking to an expansion of facilities for future supply of 2.7 million kilograms per year. Dynamit Nobel in West Germany produced approximately half a million kilograms of NTO per year at that time.

Dyno Defence Products in Norway have recently upgraded their pilot plant facilities to meet market requirements [39]. Production is now in 150 kg batches, totalling 1000 kg per month. Two classes of crystal are produced; Class 1 formed by recrystallisation has a mean particle size 300 μm , while Class 2 is produced by air-jet milling to give a mean particle size of 8 μm .

2.3 Toxicological Properties

In vivo studies have shown that both NTO and its synthetic precursor (TO) are non-toxic to mice, rats and rabbits [14, 18, 40]. NTO has LD_{50} values for oral ingestion of more than 5 g/kg in mice and rats, and is mildly irritating to rabbits when applied cutaneously. Preliminary microbiological degradation studies show that the first step in the enzymatic breakdown of NTO consisted of the reduction of the nitro group of NTO (1) to the corresponding amine (5) (Scheme 2) [18].

Scheme 2 First Step in the Enzymatic Breakdown of NTO.



2.4 Derivatives of NTO

2.4.1 Amine Salts of NTO

Synthesis of amine salts of NTO has been carried out to exploit NTO's gas generating capability for use in advanced gun propellants. Workers in the US [9, 41-45], China [46-49], Taiwan [50, 51], India [52], and Russia [53] have all conducted synthetic studies, with the derivatives well characterised.

Synthesis of the amine salts has generally been undertaken by stirring the requisite amine in an aqueous or methanolic solution of NTO. The product was recovered either by filtration or by removal of the solvent under vacuum. Twenty five salts have been synthesised from the starting amines shown in Figure 3.

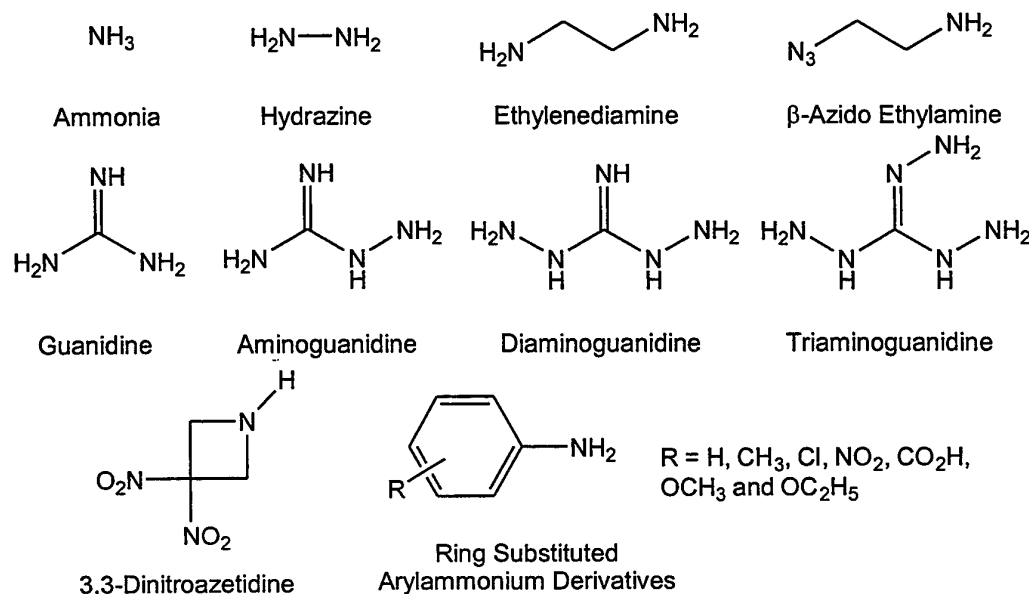


Figure 3 Amine Starting Materials For the NTO/Amine Salt series.

Little analysis of explosive performance was reported, but the NTO/amine salts were less sensitive to impact than RDX, with several exceeding the upper limit of the impact testing apparatus [41, 42, 45, 48, 51]. The salts were also insensitive in the electrostatic spark test (Table 6) [42].

Table 6 Explosive Properties of Amine NTO Salts.

Test Material	Starting Amine	Autoignition Temperature (K)	ΔH_f (kJ/mol) (Exp.)	Drop-Weight Impact Height (cm) (US)	Spark Test (3-mil foil) (J) (US)
RDX	-	488	+61.5	28	0.2
NTO	-	538.2	-59.83	no go	0.91
ENTO	Ethylenediamine	509.5	-468.2	no go	>1.0
DNAZ-NTO	3,3-Dinitroazetidine	-	-200.7	42	0.6
ANTO	Ammonia	-	-276.3	no go	>1.0
HNTD	Hydrazine	-	-158.9	92	>1.0
GuNTO	Guanidine	-	-305.2	no go	>1.0
AGNTO	Aminoguanidine	-	-177.7	no go	>1.0
DAGNTO	Diaminoguanidine	-	-87.8	252	>1.0
TAGNTO	Triaminoguanidine	-	+58.5	103	>1.0

2.4.2 Eutectics of NTO and NTO Salts

Workers at Los Alamos National Laboratory have completed preliminary examination of the ammonium and ethylenediamine salts of NTO [9]. This study paralleled encouraging earlier investigations into melt castable explosive eutectics of the ammonium and ethylenediamine salts of 5-nitrotetrazole with ammonium nitrate (AN). It was found that the corresponding salts of NTO also formed eutectics with AN which melted below 100°C (the eutectic ratios and melting points were not revealed), offering promise of melt casting from steam heated vessels.

Chinese workers report eutectic mixtures containing small amounts of NTO together with 85/15 ammonium nitrate/potassium nitrate mixture (AK) and either ethylenediamine dinitrate (EDD) or 1,6-hexamethylenediamine dinitrate (HDD) [54]. The eutectic mixtures were AK/EDD/NTO 69.97/26.09/3.94 and AK/HDD/NTO 37.55/55.51/6.94, with eutectic melting points of 103.5°C and 64.6°C respectively.

The explosive characteristics and performance of the eutectic formulations from neither laboratory have been released and they will not be discussed further in this report.

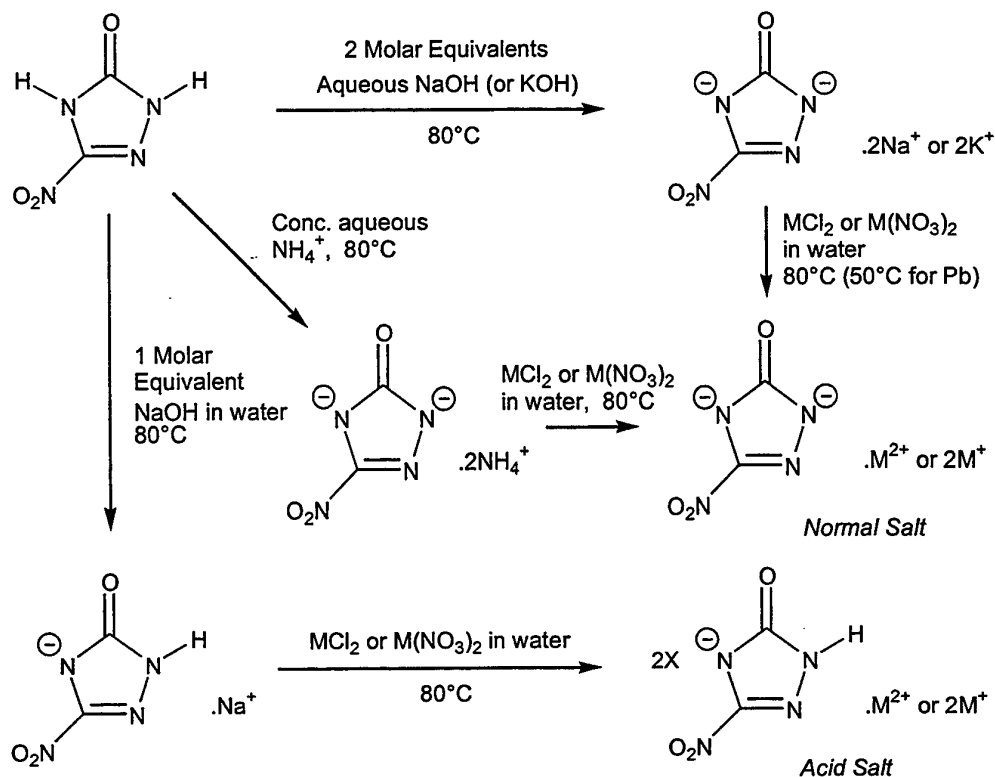
2.4.3 Metal Salts of NTO

Metal salt synthesis has been widely addressed [9, 46, 47, 51, 53, 55-59]. Work was undertaken to examine the potential of these compounds as both energetic combustion catalysts for use in propulsion systems, and for primary and secondary explosives.

Redman and Spear synthesised fifteen metal salts of NTO to evaluate their potential as primary explosives [55]. Salts included the sodium, potassium, silver, lead, mercuric, barium, cadmium, strontium, cupric, nickel, and stannous salts, as well as acid derivatives of several of these. The synthesis of the sodium and potassium salts was achieved by neutralisation of NTO with an aqueous metal hydroxide solution. The barium, strontium, stannous, and lead salts were prepared from the sodium salt, while the silver, mercuric, cadmium, cupric and nickel salts were generated from the ammonium derivative (Scheme 3).

Hazard assessment of these salts included ball and disc test, Rotter impact and thermal sensitivity tests, as well as ignition and propagation tests. Results indicated that the salts behaved like sensitive secondary explosives and would be unsuitable as primary explosives. All salts tested gave no response at the maximum drop height (30 cm) for the ball and disc test, where drop heights of 15 and 12 cm were observed for lead azide and lead styphnate respectively [60]. Only the silver salt was tested on the Rotter impact apparatus, where a F of I value of 130 (RDX 80) was found. This can be compared with lead azide and lead styphnate, common primary explosives, with F of I values 30 and 20 respectively.

Scheme 3 Synthesis of Metal Salts of NTO [55].

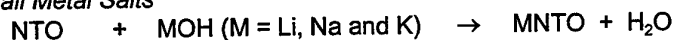


Synthesis of twenty six metal salts of NTO by Tonglai *et al.* (including many previously synthesised by Redman and Spear), was achieved directly from NTO or by further reaction of NTO salts [56]. 'S Block' metal salts were formed by reaction of NTO with alkali metal hydroxides or alkaline earth metal carbonates with NTO. Transition metal salts were formed by reaction of the metal carbonate or sulphate with the lithium or sodium salts of NTO (LiNTO or NaNTO) or with NTO itself. Rare metal salts were prepared by reaction of the metal nitrate with LiNTO, while the lead salt was formed by reaction of lead nitrate with NaNTO (Scheme 4).

Data reported for metal salts of NTO included explosive performance and hazard properties, and thermal characteristics of the salts [55, 56]. Other literature presented further thermal data including enthalpies of formation [57], autoignition temperature [51], and other thermal and spectroscopic characteristics [46, 47, 51, 58]. The critical temperature for explosion of the metal salts of NTO were 20-50°C lower than that of NTO. The temperatures of ignition of the salts were also typically slightly lower than for NTO, except the silver and copper salts, which were significantly higher.

Scheme 4 Formation of Metal Salt of NTO [56].

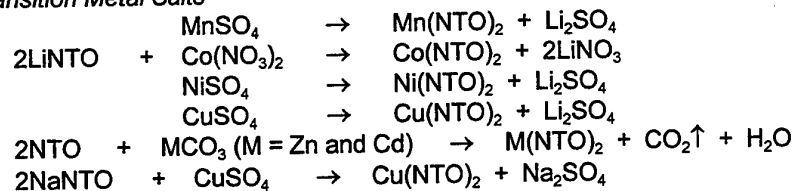
Alkali Metal Salts



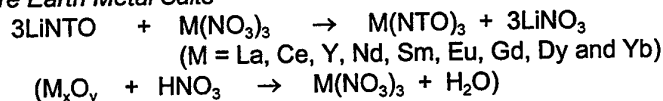
Alkaline Earth Metal Salts



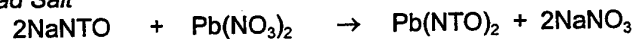
Transition Metal Salts



Rare Earth Metal Salts



Lead Salt



2.5 Thermal Analysis of NTO

2.5.1 Thermal Characterisation

Reported autoignition temperatures and heats of combustion for NTO are reasonably consistent, but the heats of formation, activation energies and heats of explosion show some variability between research groups (Table 7) [5, 6, 9, 10, 12, 26, 46, 47, 51, 53, 59, 61-63].

Table 7 Thermal Characteristics of NTO.

Energy	Value
Heat of Formation	-59.7 to -129.4 kJ/mol [5, 6, 9, 10, 12, 26, 53, 59, 62, 63]
Heat of Explosion	-392.7 to -602.2 kJ/mol [5, 6, 26]
Heat of Combustion	-943.4 to -995.7 kJ/mol [5, 6, 59, 62]
Specific Energy	119.0 kJ/mol [26]
Activation Energy	503.4 to 520.3 kJ/mol [46, 61]
Autoignition Temperature	529.6 K [47, 51, 61]

While the results shown in Table 7 have the most consistency, values obtained for the activation energy of NTO ranged from 170.1 to 520.3 kJ/mol, and appear to be markedly effected by sample and experimental conditions [64]. Williams *et al.* detected a dependence on sample confinement, with lower activation energies observed in open DSC pans, and higher values observed with sealed pans or upon flash-heating under

pressure [65]. The lower values observed were attributed to loss of the unconfined sample by sublimation.

2.5.2 DSC, DTA and TGA

The DSC and DTA traces for NTO were very simple, with a single exothermic peak with a maximum between 253 and 279°C depending on the experimental conditions used [3, 12, 25, 32, 35, 46]. Prabhakaran *et al.* also reported the presence of small exothermic peaks at 335 and 504°C [25].

TGA results show a mass loss (67%) occurring in the region between 205 and 262°C, followed by a gradual loss of the remaining mass until approximately 330°C [25, 46].

Indian researchers investigated the effect of different metal oxides and metal salt impurities added to NTO on the temperature of the DTA exotherm [25]. Lead monoxide, ferric, magnesium, cuprous and cupric oxides, titanium and zirconium dioxides, and monobasic lead stearate all catalysed the thermolysis of NTO, indicated by a decrease in the onset temperature of the exotherm. The addition of lanthanum, nickel, cerium, cobaltic and thorium oxides, copper chromite, or monobasic copper stearate lead to a higher peak position, and hence an inhibition of NTO decomposition onset.

2.6 Decomposition Studies

Many groups have examined the thermal decomposition of NTO and interest has increased over the last decade as new techniques have been developed. However, consensus still has not been reached on a single route, or even the initial step, in the thermal decomposition of NTO [25, 35, 66-83].

Extensive use of ^{15}N labelling has been employed to follow the decomposition of NTO [68-71]. This work has not revealed directly the decomposition pathways, rather the source within the NTO molecule of the atoms which make up the gaseous products. For example, nitrogen gas evolved was found to be derived mainly from the adjacent ring nitrogens (~68%), whereas a small amount was also seen to evolve from the nitro moiety (~28%) and the third ring nitrogen (~14%). Gases evolved included N_2 , N_2O , NO, and HCN, although HONO, CO_2 and CO have also been reported.

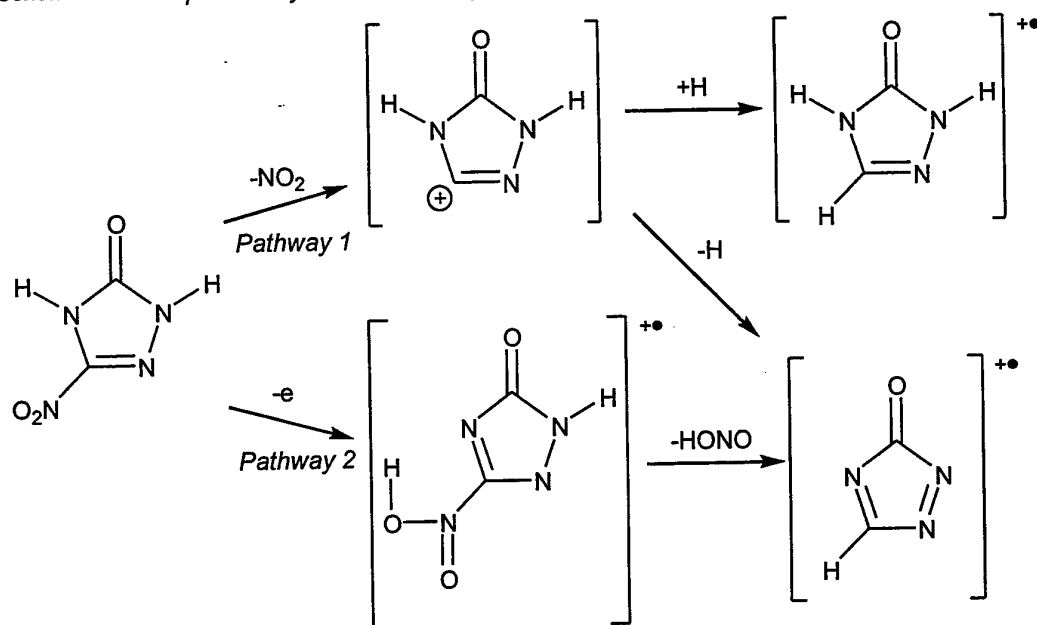
The main interest has been in the initial step of the decomposition of NTO. Thermal decomposition studies have thus far focussed on three main proposed routes; bond homolysis, nitro-nitrite rearrangement, and rupture of the triazole ring.

2.6.1 Bond Homolysis

Various studies have indicated that the first step in the thermal decomposition of NTO involves the rupture of the C- NO_2 bond (Pathway 1), and other slight variations such as the loss of HONO (Pathway 2) (Scheme 5). Workers in Stockholm were able to show

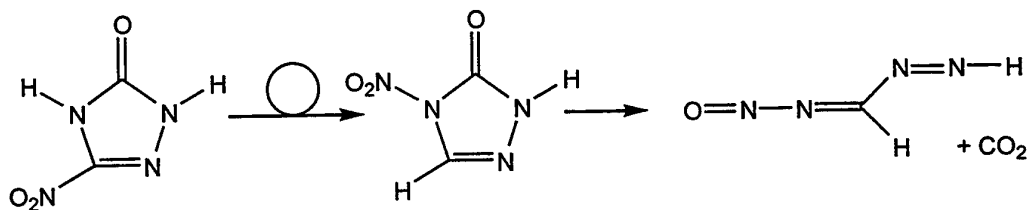
that the energy required to break the C-NO₂ bond was less than that for either of the two N-H bonds [35, 72], while MS data also showed the presence of [NO₂] and [NTO - NO₂] fragments. The work of Prabhakaran *et al.* gave further evidence of this route through the use of XRD, IR spectroscopy and thermal analysis [25].

Scheme 5 Decomposition of NTO Involving the Homolysis of the C-NO₂ Bond.



Brill *et al.* were unable to detect evidence of NO₂ or HONO gas evolution [73], but Oxley's results were consistent with the earlier studies. Observation of a DKIE (a slight increase in the rate of bond homolysis in deuterated NTO) led to the conclusion that hydrogen transfer was involved in the rate-limiting step. They suggested several mechanisms to account for the previous results, including one involving the transfer of the nitro group to the adjacent hydrogen-bearing ring nitrogen, followed by ring scission (Scheme 6), substantiating the DKIE [74, 75].

Scheme 6 Decompositions Route Proposed by Oxley *et al.*



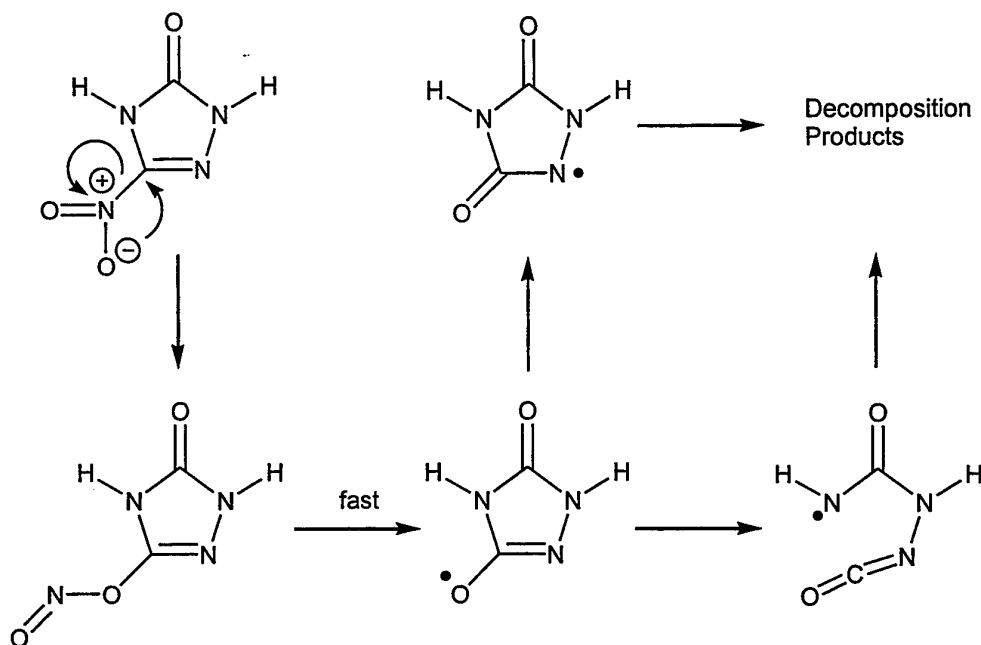
Another early study proposed that the decomposition of NTO occurred through a bimolecular reaction between the nitro group of one molecule and a ring hydrogen from another, to give the loss of HONO [76]. Using mixtures of deuterated and

undeuterated NTO and TNT to demonstrate the principle of proton abstraction, it was seen that radicals were formed when the nitro group from NTO abstracted a proton from TNT, and when a nitro group from TNT abstracted a proton from NTO.

2.6.2 Nitro-Nitrite Rearrangement

A recent study using laser ionisation MS diagnostics gave evidence of a decomposition involving the rearrangement of the nitro group to a nitrite, followed by the loss of NO, and then rupture of the ring (Scheme 7) [77]. This study used dual laser sources, with the first heating the sample and the second to effect ionisation. Mass spectrometry showed no evidence for the loss of NO₂ or HONO, but rather [NO] and the [NTO - NO] daughter ion, along with other ring fragments consistent with Scheme 7.

Scheme 7 Possible Nitro-Nitrite Rearrangement in the Decomposition of NTO.

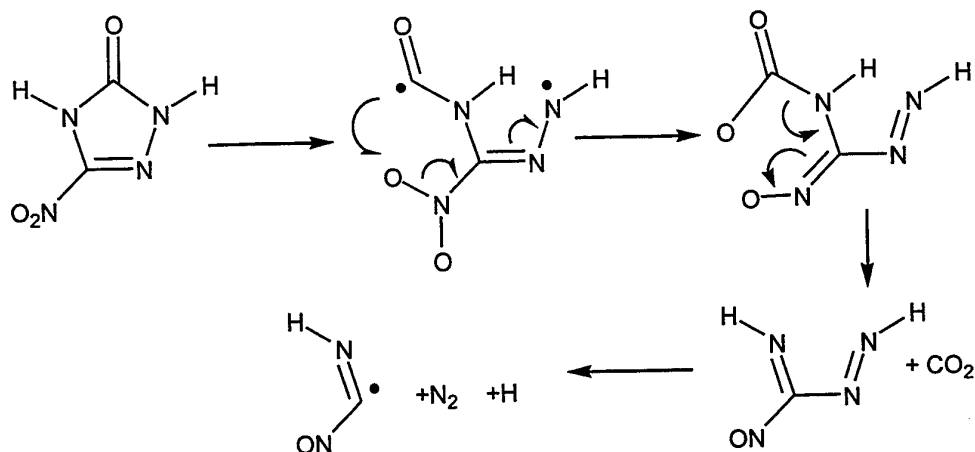


2.6.3 Rupture of the Triazole Ring, Intermolecular Route

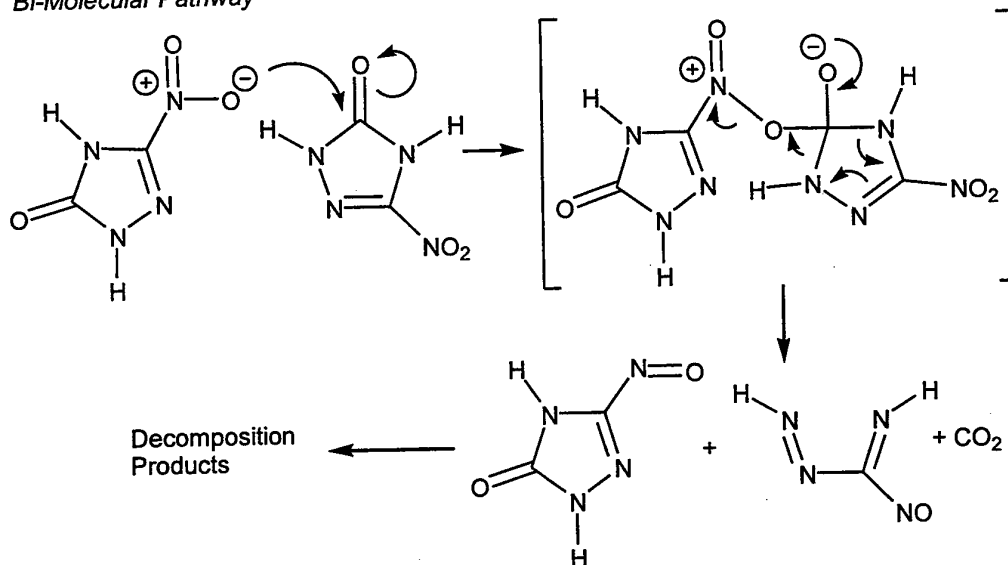
American workers initially proposed a decomposition route involving intramolecular reduction of the nitro group by the carbonyl (Scheme 8) [78]. Using IR laser pyrolysis of a thin NTO film and IR analysis of the product gases, they observed large amounts of CO₂, but no NO₂ or HONO gases. Later studies by the same workers, however, indicated that decomposition occurred *via* an intermolecular reaction, which led to the loss of CO₂ followed by N₂, and not the initially proposed intramolecular process [79].

Scheme 8 Ring Rupture Mechanism in NTO Decomposition.

Mono-Molecular Pathway



Bi-Molecular Pathway



2.6.4 Other Pathways and Information

Mass spectral studies by Garland *et al.* indicated that the initial product in the laser induced decomposition of NTO was $[NTO - O]$ [80]. This was observed by laser-induced mass spectrometry and was consistent with the loss of CO_2 noted above. It was thought that a bimolecular pathway existed where the ring-opened product attacked the nitro oxygen of another molecule. Fragments due to the loss of NO_2 and NO were seen early, however, these were not the initially formed fragments.

Pace and coworkers examined the thermal decomposition of NTO by EPR spin trapping [81]. Although this work was not aimed at determining the decomposition route, it did show the existence of the nitro anion radical, which may give further information into the possible decomposition. Later work by the same group also suggested the existence of a nitro-bearing carbon radical [82].

As part of the study by Williams, Palopoli and Brill refuting the loss of NO₂, polymeric, melon-like, cyclic azine residues were formed through the rapid thermolysis of NTO [73]. This process involved polymerisation of cyanamide-like decomposition products into tricyclic melem-like compounds and eventually the melon-like polymer. These compounds have shown promise as burn rate suppressants for use in solid propellants.

Beard and Sharma examined the decomposition of NTO samples subjected to various stimuli including impact, shock, heat and radiation [83]. It was seen that these stimuli had very little effect on the X-ray photoelectron spectra, with only a slight decrease in the nitro peak intensity. This indicated that the first step in the decomposition resulting from those stimuli, was the loss of NO₂, HONO or NO.

3. Explosive Characterisation

3.1 Vacuum Stability and Compatibility

Vacuum stability test methods differ at various research establishments. Universally, however, they indicate that NTO is thermally stable as a pure ingredient (Table 8).

Table 8 Vacuum Stability Test Results.

<i>Material</i>	<i>Temp. (°C)</i>	<i>Duration (hr)</i>	<i>Gas Evolved (cm³/g)</i>
NTO [9-11, 84]	100	48	0.2
NTO [12]	100	193	1.45
NTO [85]	110	20	0.06
NTO [3]	120	40	0.0
NTO [9-11]	120	48	0.3
NTO [12]	130	193	1.45
NTO [12]	150	193	1.7
NTO [5, 6]	150	200	Stable (Vol. Unavailable)
NTO/TNT (40/60) [84, 86]	100	48	0.08-0.1
NTO/TNT (50/50) [86]	90	40	0.3
NTO/RDX (50/50) [86]	90	40	-0.33
NTO/RDX/TNT (25/25/50) [86]	90	40	-0.1
NTO/RDX/TNT (25/25/50) [84, 86]	100	48	0.07

Several thermal decomposition studies showed some evidence of interaction in mixtures of NTO with other explosives, although the mixtures should still be regarded as thermally quite stable. Oxley found NTO and TNT were mutually destabilising [66,

74]. Experiments showed that NO_2 and ammonia and other protic species enhanced the decomposition of both NTO and TNT. Addition of TNT provided a source of hydrogen, NO_2 and HONO, each of which accelerated the decomposition of NTO.

Addition of either RDX or HMX to NTO reduces the onset for thermal decomposition of NTO [87]. Inclusion of 30% RDX or 40% HMX by weight resulted in reduction of the NTO exotherm of 50 and 25°C respectively. The presence of NTO reduced the thermal stability of RDX (20°C depression of onset temperature in RDX:NTO; 1:1), but had negligible effect on thermal decomposition of HMX, despite the structural similarities.

Conversely, Swiss and Norwegian investigations using microcalorimetric techniques have indicated good compatibility of NTO with both HMX and TNT [88].

3.2 Hazard Assessment

Direct comparison of explosive sensitiveness results obtained at different laboratories is not straightforward. Different test configurations and methods may give different results, ostensibly the same test can be carried out according to different procedures, and results of the same test carried out at the same facility but by different operators may sometimes be affected by subjective judgement. However valuable conclusions may be drawn by comparison of sensitiveness results with those for reference explosives.

3.2.1 Impact Sensitiveness

Results universally indicated that NTO is less sensitive to impact than PETN, RDX and HMX (Table 9). Preliminary results [3, 12] have indicated that NTO is more sensitive to impact than TNT, but subsequent results indicate that TNT is more sensitive [9-11, 84, 86, 89, 90].

Table 9 Impact Sensitiveness Results.

Test	NTO	PETN	HMX	RDX	TNT	TATB
Julius Peter Apparatus CSI test (J) [12]	22	-	5	4.5	30	-
Rotter Impact (Figure of Insensitivity*) [3]	80-90	40	60	80	106-115	-
Rotter Impact (Figure of Insensitivity†) [84, 86]	316	-	-	100	221	-
US Drop Impact Type 12 (cm) [9-11, 91]	>280	12	26	22	148	>320
US Drop Impact Type 12B (cm) [9, 10, 92]	293	16-32	28-38	41	-	-
US Impact Sensitivity H_{50} (cm) [89, 90]	92	13-16	32	28	80	>177
30 kg Hammer: non reaction height (m) [12, 93, 94]	>4	0.5	0.5	1	>4	>4

* RDX Reference of 80 Used, † RDX Reference of 100 Used.

3.2.2 Friction Sensitiveness

It was observed that NTO was less sensitive to friction than PETN, RDX, HMX and TNT and showed similar sensitiveness to TATB (Table 10).

Table 10 BAM* Friction Sensitiveness Tests.

	NTO	PETN	HMX	RDX	TNT	TATB
SNPE Data (N) [93, 94]	>353	125	175	133	~353	>353
South African Data (N) [84, 86]	>353	-	-	247	>353	-
SNPE Data (N) [12]	>353	-	100	113-174	300	-

* BAM Friction = Julius Peters, Bundesanstalt für Materialprüfungen (BAM) High Friction Sensitivity Tester

In work by Graham *et al.*, it was seen that ammonium perchlorate (AP) produced high friction sensitiveness in cast-cured formulations [95]. To alleviate this problem, several replacement solid oxidisers were examined including NTO. It was seen that NTO both improved the sensitiveness, and improved the calculated performance as predicted by the TIGER computer code.

3.2.3 Electrostatic Discharge Sensitiveness

NTO is less sensitive to ignition by electrostatic discharge than RDX and TNT (Table 11).

Table 11 Electrostatic Sensitiveness Testing.

	NTO	RDX	TNT
Australian Data (J) [3]	>4.5	4.5	-
South African Data (J) [84, 86]	15	0.225	0.138
SNPE Data (J) [5, 6]	>0.726	-	-
Czech Data (J) [96]	8.98	2.49	6.85
US Data (3 mil, J) [9-11]	0.91	0.22	-
US Data (10 mil, J) [9-11]	3.40	0.55	-

3.2.4 Thermal Sensitiveness

Various research groups measured ignition sensitivity to thermal stimuli, generally by heating a known mass of sample at a constant rate and recording the temperature at which thermal runaway occurs. It was found that NTO was less sensitive to heating than RDX, HMX and PETN, but was more sensitive than TATB (Table 12).

Table 12 Thermal Sensitivity Ignition Tests.

	NTO	PETN	HMX	RDX	TNT	TATB
Temp. of Ignition (SNPE) (°C) [12, 93, 94]	280	190	270	220	290	350
Temp. of Ignition (MRL) (°C) [3]	258	149	-	216	240	-
Henkin Critical Temp. (°C) [9-11, 92]	237	175	210	219.6	261	-
Henkin Critical Temp. (°C) [62]	216	-	-	-	-	-

3.2.5 Shock Sensitivity

Shock sensitivity of NTO has only been reported by French workers [12, 93, 94] using the NOL Large Scale Gap Test. This involved detonation of a donor booster charge separated from the acceptor sample charge by a number of 0.19 millimetre thick polymethylmethacrylate attenuation discs [91]. It was seen that NTO was less sensitive to shock initiation than RDX, HMX and PETN, but more sensitive than TATB (Table 13).

Table 13 Shock Sensitivity Test Results.

	NTO	PETN	RDX	HMX	TATB
SNPE Results (No. of Discs) [12, 93, 94]	260	330	310	305	190

3.2.6 Machining of NTO Charges

High speed machining tests at Los Alamos National Laboratory on pressed samples of NTO and NTO/TNT (50/50) utilised standard drilling test procedures [14]. Forty 0.25 inch diameter holes were drilled into each charge with a drill speed of 2260 rpm and at a penetration rate of 0.025 inches per revolution. As NTO is water soluble, it was required that the charges were machined dry. Both the NTO and NTO/TNT charges showed no reaction during testing.

3.3 Explosive Performance

3.3.1 Detonation Velocity

FORTTRAN-BKW has been used for French predictions of the velocity of detonation (VoD) of NTO, and for comparison with reference explosives (Table 14) [12, 93, 94]. The VoD of NTO was less than those of RDX and HMX, comparable with that of PETN, and greater than that of TATB. US results [89] using CHEETAH and Czech work [96] using the Kamlet Jacobs method [97] were consistent with these calculations.

Table 14 Detonation Velocity Calculated by Various Research Groups.

	NTO	HMX	RDX	PETN	TATB
French Data (m/s) [12, 93, 94]	8510	9100	8850	8500	8000
Czech Data (m/s) [96]	8590	9130	8890	8930	-
American Data (m/s) [89]	8560	9300	8930	-	8100

Using confined NTO charges with an internal diameter of 4.1 cm, Chapman *et al.* recorded VoDs of 8020 to 8200 m/s as the charge density was increased from 93.3 to 97% TMD [14].

SNPE research examined the VoD of unconfined pressed NTO (Classes I and IV) at varying densities and charge diameters [36]. Consistently, charges pressed from the

smallest particle size (Class IV) had higher VoD than those from the larger Class 1 at the same densities and charge diameters. For each class VoD increased with density. Stable detonation of the larger Class 1 was not achieved below 15mm.

In a separate study, the VoD of NTO was also measured in copper detonating cords of internal diameter 4 mm [93, 94]. At a density of 1.69 g/cm³ the VoD was measured at 7400 m/s, and at 1.71 g/cm³, 7770 m/s, consistent with other experimental values. This diameter was well below the critical diameter of NTO (see Section 3.3.3 below), and heavy confinement by the copper is therefore assumed.

3.3.2 Detonation Pressure

Plate dent tests were used by Spear *et al.* to determine the relative detonation pressure of NTO with respect to RDX and tetryl [3]. Using both confined and unconfined charges, it was found that the pressure output of NTO was 85% that of tetryl at 12.7 mm diameter, and 88.5% at 15.9 mm diameter. At 12.7 mm, the pressure output was 76% that of RDX, indicating poorer performance than both RDX and tetryl, but at higher diameters, performance approached that of RDX.

Detonation pressure was calculated and measured by Lee *et al.* for unconfined charges at varying densities and diameters, again using the plate dent test [9-11]. Calculated values were derived from the BKW equation of state and a comparison was made to RDX and TATB at the largest diameter (Table 15).

Table 15 Detonation Pressures Calculated and Measured from Plate Dent Tests [9-11].

Explosive	Charge Density (g/cm ³)	Charge Diameter (cm)	Pressure (GPa) Measured	Pressure (GPa) Calculated (BKW)
NTO	1.93 (100% TMD)	-	-	34.9
	1.781 (92.2% TMD)	4.13	27.8	28.4
	1.853 (96% TMD)	4.13	26.0	31.6
	1.782 (92.3% TMD)	2.54	24.0	28.4
	1.855 (96.1% TMD)	2.54	Failed	31.6
	1.759 (91.1% TMD)	1.27	25.0	27.1
	1.824 (94.5% TMD)	1.27	Failed	-
RDX	1.767 (97.8% TMD)	4.12	33.8	34.8
TATB	1.87 (96.5% TMD)	4.12	27.7	31.3

3.3.3 Critical Diameter

Researchers at Los Alamos National Laboratory determined the critical diameter of pressed NTO using a rate stick, consisting of a series of charges of decreasing diameters, initiated at the larger end using a detonator and a booster. The diameter at which detonation failed gave a crude estimate of the critical diameter. Refinement of the charge diameters gave a more accurate indication of the critical diameter. The

critical diameter of NTO at 96.8% TMD was found to be close to one inch (25.4 mm) [14]. As a comparison, RDX and tetryl have critical diameters less than 2 mm [3].

Studies at Eglin AFB also examined the critical diameter of NTO pressed to 94.2% TMD using a 76.2 mm diameter cone [62], again initiated from the large end using a detonator and booster. The detonation velocity was measured using piezoelectric pins and a streak camera. Shock velocity was plotted against diameter and the failure point defined as 90% of the steady state velocity. Calculations gave the critical diameter as less than 25.40 mm, consistent with the results from Los Alamos National Laboratory.

At this laboratory, the critical diameter was not measured directly, but a value close to 12.7 mm at 90% TMD was inferred from experimental firings on pressed charges using an exploding bridge wire detonator and tetryl booster [3].

4. Formulations Containing NTO

4.1 Melt-Cast Formulations

Work on melt-cast formulations has been undertaken predominantly for the USAF, involving several mixtures of TNT and NTO (some aluminised) designated TNTNO formulations (Table 16) [62, 66, 98-106]. The composition TNTNO IV was selected for further work, and was later designated AFX-644. A subsequent study examined the use of emulsifiers and processing aids to avoid exudation problems associated with the low melting point wax D2, with reformulation of AFX-644 to give a replacement AFX-645 [104-106]. D2 Wax (Indramic-170C 84%, Nitrocellulose 14% and Lecithin 2%) is commonly used in Composition B, but only at the level of 1%. The concentration of wax was substantially increased in the TNTNO formulations to modify the material properties of the TNT matrix, but pressurised heating experiments on AFX-644 showed

Table 16 Melt-Cast Formulations Containing NTO.

Designation	NTO	TNT	Additives	Binder
TNTO [62]	50	50	-	-
TNTO/D2 [62]	52	42	-	6 (D2 Wax)
TNTO/OD2 [62]	52	42	-	6 (OD2 Wax*)
TNTO O [62]	38	40	16 (Aluminium)	6 (D2 Wax)
TNTO I [62]	42	34	19 (Aluminium)	5 (D2 Wax)
TNTO II [62]	42	32	19 (Aluminium)	7 (D2 Wax)
TNTO III [62]	42	30	19 (Aluminium)	9 (D2 Wax)
AFX-644 (TNTO IV) [62]	40	30	20 (Aluminium)	10 (D2 Wax)
AFX-645 [100]	48	32	12 (Aluminium)	8 (I-800 Ganex)
GD-1 [88, 107, 108]	65	35	-	-
GD-2 [88, 107, 108]	35	35	30 (HMX)	-
'South African 1' [84, 86]	40	60	-	-
'South African 2' [84, 86]	25	50	25 (RDX)	-

* - OD2 Wax = Ozokerite Wax 85%, Nitrocellulose 14%, Lecithin 1%

8% exudation (mainly wax). Substitution with Indramic-800 wax/Ganex WP-660 (98.5/1.5) decreased exudation to 0.43%, while ensuring minimum growth following thermal cycling.

Collaborative studies were carried out between Switzerland and Norway (the GD series), leading also to a formulation including HMX [88, 107, 108]. A parallel South African study used RDX rather than HMX (Table 16) [84, 86].

4.1.1 Performance and Characterisation

Velocity of detonation and critical diameter measurements for several of the US formulations are shown in Table 17 [62, 100, 103]. The VoD of AFX-644 and AFX-645 were found to be 97% and 101% that of a Tritonal standard (80% TNT, 20% Aluminium), respectively.

Table 17 American Performance Results

<i>Formulation</i>	<i>Density (g/cm³)</i>	<i>Velocity of Detonation (m/s)</i>	<i>Critical Diameter (mm)</i>
TNT	1.74	7340	16
TNT/D2	1.54	6470	<25
TNT/OD2	1.61	6900	<25
TNT I	1.76	6670	25-51
TNT II	1.74	6840	32-35
AFX-644	1.70	6960	41-43

VoD of the two GD series formulations, both measured and calculated, is presented in Table 18 below [88, 107, 108]. These compositions, due to the unfavourable crystal shape of NTO available at that time, were found to have high viscosities resulting in voids and difficult processing. As these formulations were investigated for application to shaped charges, performance was deemed low, and further work was not undertaken on these compositions, although this performance exceeds that of the TNT formulations noted above.

Table 18 Performance Data of Melt-Cast GD Series Formulations.

<i>Designation</i>	<i>Density (g/cm³)</i>	<i>Percentage of Theoretical Mean Density (TMD)</i>	<i>Velocity of Detonation (Calc.) (m/s)</i>	<i>Velocity of Detonation (Exp.) (m/s)</i>
GD-1	1.750	96.9	7662	7510
GD-2	1.761	97.9	7994	7870

South African performance data was based on measured and calculated VoD values [86]. Both formulations showed poorer performance (ca. 6-8%) than an RDX/TNT (50/50) standard (7280 m/s and 7454 m/s cf. 7900 m/s for the standard). Fragment velocity measurements on a 155 mm round showed fragment velocities of 1569 m/s (NTO/TNT) and 1718 m/s (NTO/TNT/RDX) [84]. Both showed lower performance than that the 50/50 TNT/RDX filled equivalent (1825 m/s).

4.1.2 Compatibility Testing and Other Factors

South African compatibility tests, focussed on the compatibility of NTO with TNT and with both RDX and TNT together, which found that all components were compatible, were described in Section 3.1 [84, 86].

Results from the US Chemical Reactivity Test (CRT) on different TNTO formulations, with and without wax, indicated no incompatibilities [62]. Gas volumes recorded were generally consistent with weighted averages of TNT and NTO, while slightly higher values were seen in the presence of D2 wax (Table 19). However reference must be made to the work of Oxley *et al.* who demonstrated marked destabilisation of NTO/TNT mixtures (Section 3.1) [66, 74].

Table 19 US CRT Results.

Sample	Volume of Gas Evolved (cm ³ /g)
TNT	0.16
NTO	0.02
TNTO	0.09
TNTO/D2	0.29
TNTO O	0.21
TNTO II	0.35
AFX-644	0.37

4.1.3 Small Scale Hazard Assessment

Impact testing conducted in the US (Bureau of Mines instrument, 5 kg drop weight) showed all formulations to be less sensitive to impact than NTO or TNT alone, with the majority beyond the upper limit of the instrument (Table 20) [62]. South African data showed both formulations to be more sensitive to impact than NTO, but less sensitive than RDX (Table 21) [84, 86].

Table 20 US Sensitiveness Testing.

Designation	H _{50%} (cm)	BAM Friction (N)	Electrostatic Discharge (J)
TNT	54.5	35.3	0.062
NTO	53.5	176.5	0.062
TNTO	91.5	41.2	0.062
TNTO/D2	>200.5	53.0	0.062
TNTO/OD2	>200.5	-	-
TNTO O	>200.5	41.2	0.040
TNTO I	>200.5	-	-
TNTO II	>200.5	53.0	0.040
TNTO III	>200.5	-	-
AFX-644	>200.5	60.8	0.040

Table 21 South African Melt Cast Formulation Hazard Data.

Sample	Composition	Impact Sensitivity (F of I)	Friction Sensitivity (N)	Electrostatic Discharge (mJ)
NTO	-	316	>353	15000
TNT	-	221	>353	138
RDX	-	100	247	225
NTO/TNT	40/60	276	>353	170
NTO/RDX/TNT	25/25/50	186	>353	170

US friction testing showed that all formulations were more sensitive to friction than NTO but less than TNT (Table 20) [62, 99]. Friction sensitiveness of compositions examined in South Africa were all beyond the upper limit of the instrument (Table 21) [84, 86].

Workers at Eglin Air Force Base studying TNTO compositions found that the aluminised formulations were more sensitive to electrostatic discharge than NTO, TNT, and the non-metallised formulations, which all presented similar values (Table 20) [62, 99]. South African electrostatic discharge tests indicated that the formulations were less sensitive than TNT, but were more sensitive than RDX and NTO (Table 21) [84, 86].

Apparent inconsistencies between the sensitiveness data reported in Tables 10, 20 and 21, notably that for NTO and TNT, highlight the difficulties in making absolute comparisons. However the general trends remain the consistent. The South African value for the electrostatic sensitiveness of NTO is remarkable, but was given without comment. It may represent a typographical error.

4.1.4 Munition Hazard Assessment

US testing on melt cast formulations in accordance with the UN HD 1.6 test series has been extensive [62, 99-102, 109, 110]. Tests on the TNTO series formulations showed that all compositions were extremely insensitive to hazards stimuli, and passed most tests undertaken [62, 98]. AFX-644 has passed the entire HD 1.6 series tests on the complete Mk-82 general purpose bomb [62, 109]. AFX-645 was later examined and although passing the HD 1.6 substance tests, was only able to achieve a HD 1.2 classification [62, 99, 100, 102]. It was thought that with improved bomb case venting, hazard division 1.6 would be achieved for the complete munition. AFX-645 has been seen to be substantially less sensitive to shock than the current explosive fillings used in Mk 82 bombs, without compromising performance [101].

Vulnerability testing on the South African compositions included thermal cycling, drop tests on a steel plate, fuel fire tests, sympathetic detonation and bullet impact tests, all carried out on filled 76 mm and 155 mm shells [84, 86]. Freshly filled shells had a loose, soft, waxy filling with no anchorage to the walls. After thermal cycling, the filling was anchored to the walls, and had a hard, brittle structure. As a reflection of this change, freshly filled shells all showed cracks and separation after drop testing,

whereas in the thermally cycled shells the filling remained anchored to the walls. No mention was made of the effects of this thermal cycling on setback initiation during gun-firing.

Fuel fire testing of 76 mm rounds was encouraging. The most vigorous result with NTO/TNT was propulsive ejection of the end plug, with no high order events [84, 86]. The NTO/RDX/TNT filled round showed slightly more severe results, with pressure rupture followed by deflagration. In the 155 mm round the NTO/TNT filling gave pressure bursts, while NTO/RDX/TNT filled rounds gave low order detonations.

Sympathetic detonation experiments were carried out to determine the distance required between adjacent 155 mm shells such that no reaction, or at most, deflagration was seen [84, 86]. Using TNT donor shells it was observed for the NTO/TNT formulation all distances less than or equal to 120 mm resulted in detonation of the acceptor charge. A separation of 130 mm resulted in an explosion, and 140 mm separation generated a deflagration. At a distance of 150 mm no reaction was detected. For the NTO/RDX/TNT composition, 150 mm resulted in detonation, 200 mm separation an explosion, and a 400 mm separation gave a deflagration.

Bullet impact tests on 76 mm and 155 mm rounds filled with NTO/TNT resulted in burning with the exception of one 155 mm round which underwent deflagration [84, 86]. Reactions for the NTO/RDX/TNT formulation were more severe. For both the 76 mm and 155 mm, one test resulted in burning and pressure rupture, while the second produced deflagration.

4.1.5 Demilitarisation

Ross *et al.* examined the laboratory scale destruction of AFX-644 using a hydrothermolysis technique [111]. The explosive was loaded into an autoclave containing water, pressurised to several hundred atmospheres and heated to 300°C for 4 hours. Post process analysis of gases, solids and aqueous phase was carried out for nitrogenous and carbonaceous products. Nitrogen gas, nitrite anion and a trace of ammonium cation, and 10% of an unidentified solid residue, accounted fully for the nitrogen content. Gas phase analysis identified carbon monoxide and dioxide, while the aqueous phase contained formate and acetate anions. The unidentified solid residue accounted for about 50% of the initial carbon, but a total of only 81% was recovered.

4.2 PBX Formulations

NTO-based PBX development has been performed predominantly at SNPE, where much work has been undertaken on the "B series" compositions (Table 22) [5, 12, 109, 112-120].

Table 22 French "B series" and American PBXW Compositions.

Name	NTO	RDX	HMX	AP	Aluminium	Binder
B 2214 [12, 109, 112-116, 119]	72	-	12	-	-	16 (HTPB)
B 2225 [5]	#	#	-	-	-	14.5 (HTPB)
B 2233 [118, 120]	31	-	6	28	10	15 (HTPB)
B 2236	#	-	#	-	-	# (Inert)
B 2245 [112]	8	12	-	43	25	12 (HTPB)
B 2248 [112, 113, 119]	46	-	42	-	-	12 (HTPB)
B 3017 [113, 115]	74	-	-	-	-	26 (Energetic#)
B 3021 [112, 113, 115, 117]	50	25	-	-	-	25 (Energetic#)
PBXW-121 [121]	63	10	-	-	15	12 (HTPB)
PBXW-122 [38, 122]	47	5	-	20	15	13 (HTPB)
PBXW-124 [122]	27	20	-	20	20	13 (HTPB)
PBXW-125 [122]	22	20	-	20	26	12 (HTPB)
PBXW-126 [122, 123]	22	20	-	20	26	12 (Polyurethane)

Undisclosed

Work on B 3021 was discontinued at an early stage, despite the high performance and low sensitivity, due to the high costs involved in the manufacture of shaped charges using this composition relative to cyclotol [117]. Studies involving B 2233 were directed towards its use as the less sensitive outer layer in a dual formulation warhead, in which B 2237 (HMX, AP, Al and binder) was used as the inner, more sensitive (and more powerful) formulation [118]. Each variation in charge configuration passed the sympathetic detonation test in a 152 mm charge, although results were not given for performance or other hazard tests.

US PBX work has generated five formulations containing NTO (Table 22) [38, 121-123], of which several have been assessed according to the UN test series 7. The US Navy has also examined two formulations consisting of 28% NTO, 56% HMX and HTPB binder each using a different HMX particle size [124]. No further information has been available.

Research in the UK towards insensitive PBX formulations involved the use of NTO with energetic nitramines [119, 125, 126]. To counter the small loss in performance as NTO replaces the more energetic nitramine, the energetic binder PolyNIMMO was incorporated with the energetic plasticiser K10, and HMX substituted for RDX, for CPX 412 and 413 (Table 23). CPX 413 passed the HD 1.6 test series, but further testing is required before service use. Development has been directed towards use of CPX 413 in underwater blast charges [124].

Little information is available regarding German formulations, although one candidate insensitive high explosive was examined as part of the Four Power Air Senior National Representative Co-operative Long Term Technology Project on Insensitive High Explosives (ASNR LTTP on IHE) [119]. The formulation, designated HX 310, contained NTO, HMX, and NG (Table 23).

Table 23 UK, Swiss and Norwegian, German and Canadian Formulations [107, 108, 119, 124-127].

Designation	NTO	HMX	Additives	Binder	Energetic Plasticiser
CPX 412 [125]	50	30	-	10 (PolyNIMMO)	10 (K10 [†])
CPX 413 [119, 124, 125]	45	35	-	10 (PolyNIMMO)	10 (K10)
CPX 450* [126]	40	20	20 (Aluminium)	10 (PolyNIMMO)	10 (K10)
CPX 455* [126]	40	20	20 (Aluminium)	10 (PolyNIMMO)	10 (K10)
CPX 458 [126]	30	30	20 (Aluminium)	10 (PolyNIMMO)	10 (K10)
CPX 459 [126]	20	40	20 (Aluminium)	10 (PolyNIMMO)	10 (K10)
CPX 460 [126]	27.5	27.5	25 (Aluminium)	10 (PolyNIMMO)	10 (K10)
GD-3 [107, 108]	72	12	-	16 (HTPB)	-
GD-5 [107, 108]	40	43	-	7 (PGA)	10 (BDNPA/F)
HX 310 [119]	25	47	10 (NG)	18 (HTPB)	-
CHN-037 [127]		76	-	24 (GAP)	-

* Different grades of HMX used, † K10 = Dinitroethylbenzene/2,4,6-Trinitroethylbenzene 65/35

4.2.1 Performance and Characterisation

The limited data available on the performance of the French "B series" PBX compositions are presented below (Table 24) [12, 112-115, 119].

Table 24 French Performance Data.

Formulation	Density (g/cm ³)	Detonation Velocity (m/s)	Critical Diameter (mm)
B 2214 [12, 112, 114, 115, 119]	1.63	7495	.35 (confined), 65 (unconfined)
B 2245 [112]	1.81	5150	-
B 2248 [119]	1.70	8130	11
B 3017 [113, 115]	1.75	7780	10-15
B 3021 [112, 115]	1.77	8100	<10

Results for PBXW-126 included a VoD of 6000 m/s, detonation pressure of 160 kbar and unconfined critical diameter of less than three inches [128]. A second study, however, measured the VoD at 6470 m/s at a density of 1.80 g/cm³ [122]. The peak pressure generated by PBXW-126 was found to be 1.29 times that of TNT, and 1.22 times that of PBXN-109. Impulse generated was 1.06 and 1.25 times that of TNT and PBXN-109 respectively.

Performance data for the remaining European PBXs is presented in Table 25 [107, 108, 119, 125, 129]. Shaped charge penetration performance of GD-5 is 18% lower than that of LX-14 (95.5% HMX, 4.5% Estane).

Table 25 Performance of Remaining Formulations [107, 108, 119, 125, 126, 129].

	Density (g/cm ³)	Velocity of Detonation (m/s)	Critical Diameter (mm)
GD-3 [107, 108]	-	6838	-
GD-5 [107, 108]	-	8035	-
HX 310 [119]	1.57	7750	≤10
CPX 412 [125]	1.66	7200	-
CPX 413 [119, 125]	1.74	8150	10
CPX 450 [126, 129]	1.85	7762*	-
CPX 458 [126, 129]	1.85	7676*	-
CPX 459 [126, 129]	1.86	7761*	-
CPX 460 [126, 129]	1.88	6420	-

* These values are thought to be high due to the CHEETAH programs optimisation of aluminised formulations

4.2.2 Compatibility Testing

It was suspected that the low pKa (3.76) of NTO might create compatibility and ageing problems, particularly with TNT and in various binder systems in which free radical curing by isocyanates might be inhibited by the NTO [40, 89].

Desmodur N-100 is commonly used in UK explosive formulations, and no gross incompatibilities are found in cured formulations containing this material and NTO [125]. However compatibility testing (100°C, 40 and 48 hours) of NTO with Desmodur N-100 showed substantial incompatibilities, with large gas volumes evolved for each experiment [130], although only modest gas volumes were evolved from mixtures of NTO with isophorone diisocyanate (IPDI) [107]. Vacuum stability tests (100°C, 48 hours) on both HX 310 and CPX 413 showed evolution of only minor amounts of gas (0.47 cm³/g and 0.52 cm³/g respectively) [119]. Vacuum stability tests (120°C, 22 hours) on PBXW-126 showed no incompatibilities, with only 0.03 cm³/g gas evolved [123].

4.2.3 Small Scale Hazard Assessment

Studies on HX 310 and CPX 412 and 413 [119, 125] included determination of the impact and friction sensitiveness and thermal stability, together with the small scale burning test for the CPX compositions, all according to the UN Series 3 tests. Acceptable results were seen for all compositions, with CPX 412 proving slightly less sensitive to hazards stimuli than CPX 413.

PBXW-126 has impact sensitiveness intermediate between TNT and HMX, but is markedly more sensitive to friction (Table 26) [123], possibly due to the presence of AP [131]. No response was seen to a 1 J electrostatic discharge.

Table 26 Sensitiveness Testing of PBXW-126.

Sample	Impact Sensitiveness H_{50} (cm)	BAM Friction (N)	Electrostatic Discharge (J)
TNT	148	113.7	no reaction
HMX	32	113.7	no reaction
PBXW-126	95.7	39.2	no reaction

Small scale testing of uncured GD-5 showed the formulation had moderate sensitiveness to friction and low sensitiveness to both impact and electrostatic discharge [107].

Extended large scale gap tests on three French formulations showed all three to be less sensitive to shock than an HMX reference, ORA86 (86% HMX, 14% Polyurethane Binder) (Table 27) [113, 115]. Similar results were seen for CPX formulations [126, 129].

Table 27 Extended Large Scale Gap Test Results.

Test Formulation	Thickness of Barrier (mm)	Pressure (kbar)
ORA86 [113]	80	30
B 2214 [113]	40	80
B 3017 [113]	35	90
B 3021 [113]	60	-
CPX 413 [126]	33	-
CPX 450 [126, 129]	26	-
CPX 455 [126, 129]	28	-
CPX 460 [129]	33	-

4.2.4 Munition Hazard Assessment

Extensive testing has been undertaken on the various PBX formulations following UN series 7 test procedures in unreported hardware (Table 28) [12, 107-110, 112-114, 116, 119, 122, 125, 128, 132].

French work involved two experimental formulations consisting of NTO and HMX with either a polyurethane or polybutadiene binder [132]. The composition containing polyurethane was subjected to bullet impact testing with bullet impact velocities of 930 or 1140 m/s employed. At the lower velocity no reaction was seen, whereas at 1140 m/s a combustion reaction was observed. The composition containing polybutadiene was subjected to shock sensitivity tests, at diameters of 40 and 75 mm. Results indicated that the formulation was considerably less sensitive to shock than the Composition B and TNT references used.

4.3 Pressed Formulations

As part of the collaboration between Switzerland and Norway, six pressed formulations containing NTO were formulated (Table 29) [107, 108]. Moulding

Table 28 UN Series 7 Tests on Various Formulations.

	B 2214	B 2245	B 2248	B 3017	B 3021	PBXW -126	HX 310	GD-5	CPX 413
Cap Test	✓	✓	✓	✓	✓	-	✓	-	✓
Gap Test	✓	✓	✓	✓	✓	-	✓	-	✓
Friability	✓	✓	✓	✓	✓	-	✓	-	✓
Susan*	-	-	-	-	-	-	✓	-	✓
Bullet Impact*	✓	✓	✓	✓	✓	✓	✓	✓	-
External Fire Slow	✓	✓	✓	✓	✓	✓	-	✓	-
Cook-off	✓	✓	✓	✓	✓	✓	✓	✓	✓
Sympathetic Detonation	✓	-	-	✓	✓	✓	✓	-	✓
Fragment Impact	✓	-	-	✓	-	✓	-	✓	-

✓ Acceptance Criterion met, - test not undertaken, * Alternative methods to Friability test

powders GD-9 and GD-10 were both prepared using a solvent evaporation method, whereas GD-11 to GD-14 were all formed using a water slurry technique. French studies generated an additional pressed formulation [93, 109].

Table 29 Pressed Formulations.

Designation	NTO	HMX	BDNPA/F	Binder
GD-9 [107, 108]	47.5	47.5	2.5	2.5 (Cariflex 1101)
GD-10 [107, 108]	48.8	48.8	-	2.4 (Cariflex 1101)
GD-11 [107, 108]	48	48	-	4 (Cariflex 1101)
GD-12 [107, 108]	48	48	-	4 (Cariflex 1107)
GD-13 [107, 108]	48	48	-	2/2 (Hy Temp/DOA)
GD-14 [107, 108]	48	48	-	4 (Estane)
'French 1' [93, 109]	55.5	37	-	7/0.5 (Kelf/Graphite)

4.3.1 Performance and Characterisation

VoD for the Swiss/Norwegian formulations, as well as shaped charge performance (in comparison with LX-14), are presented in Table 30 [107, 108]. Performance generally

Table 30 Performance of Swiss and Norwegian Formulations [107, 108].

Designation	Velocity of Detonation (Calc.) (m/s)	Percentage of TMD	Velocity of Detonation (Exp.) (m/s)	Shaped Charge Performance Loss (%)
GD-9	8280	97.8	8360	-
GD-10	8352	97.6	8430	-
GD-11	8187	-	-	-
GD-12	8174	95.7	7829	-15.5
GD-13	8275	95.2	8520	-15.5
GD-14	8268	94.7	8458	-10.5

exceeded that calculated. However performance of GD-12 and GD-13 differed by as much as 10%, even though the energetic materials content (96% of the total composition) was unchanged. This observed difference in performance is possibly a consequence of variation in charge quality rather than composition [108].

4.3.2 Small Scale Hazard Assessment

Of the GD series examined, the compositions formed by solvent evaporation (GD-9 and 10) proved to be more sensitive than those formed by the water slurry technique (GD-12 to 14, Table 31) [107]. The differences in sensitiveness may be a combined result of the pressing powder formation method and the slight increase in energetic materials content seen for GD-9 and 10. Testing of the French pressed formulation showed it to be less sensitive to impact than HMX or RDX, but more sensitive than NTO and TNT. The formulation was also seen to have lower sensitiveness to friction than HMX, RDX and PETN, but slightly higher sensitiveness than NTO, TATB and TNT [93, 94].

Table 31 Hazard Testing Results of Selected GD Formulations.

<i>Formulation</i>	<i>BAM Impact (J)</i>	<i>BAM Friction (N)</i>	<i>Electrostatic Discharge (J)</i>
GD-9	4	192	0.320
GD-10	3	192	0.180
GD-12	7.5	252	-
GD-13	7.5	252	-
GD-14	7.5	213	-

4.3.3 Munition Hazard Assessment

Results for several of the UN Test Series 7 HD 1.6 (EIDS) tests for the formulations GD-12, 13 and 14 are shown in Table 32 [108]. All three passed both cook-off tests and bullet impact however, composition GD-13 failed fragment impact, giving a partial detonation.

Table 32 UN Series 7 Tests on Selected GD Series Formulations.

<i>Formulation</i>	<i>Slow Cook-off</i>	<i>Fast Cook-off</i>	<i>Bullet Impact</i>	<i>Fragment Impact</i>
GD-12	V	V	V	N.R.
GD-13	V	V	N.R.	II
GD-14	IV	V	IV	IV

I = Detonation, II = Partial Detonation, III = Explosion, IV = Deflagration, V = Burning, N.R. = No Reaction

5. Discussion and Recommendations

NTO-based explosive formulations have been considered for a variety of applications. The South African research has been directed towards melt-cast NTO/TNT

compositions and variants for shell fillings, and the USAF emphasis has been on related formulations for insensitive bomb fillings. French and ASNR work is directed towards a variety of insensitive PBXs, mainly for IM purposes; UK and US Navy research is directed towards PBXs for general purpose and underwater explosive formulations. The Swiss-Norwegian effort is directed towards melt-cast and PBX formulations for use in shaped charges.

The use of explosive formulations based on NTO presents potential material options to meet the operational needs of the ADF and to satisfy the requirements of Insensitive Munitions (IM). In particular, the use of melt cast NTO/TNT based compositions such as AFX-644 and AFX-645 may provide viable IM-compliant options for the RAAF for Mk 80-series bombfills, drawing on Australian industry's well established familiarity with melt cast TNT-based explosives filling technology. Application of these explosives to give HD 1.6 stores could also have important consequences for storage and transport. A program of research and development in NTO/TNT explosives is recommended to develop high quality charges to be assessed as insensitive alternatives to current TNT based explosives.

An ample supply of imported NTO is available for R&D purposes. This material must be fully characterised, and its explosive sensitiveness confirmed in Australian tests. Note should be made of the apparent inconsistency of compatibility studies of NTO with TNT and nitramines, and Australian tests will be required to resolve this issue. Experimental castings of NTO/TNT should then be prepared, in order to optimise rheology, sedimentation, casting quality and composition, while evaluating both explosive performance and charge sensitivity. Further ingredients can then be incorporated to enhance air blast and to modify the materials properties of the crystalline TNT matrix. Finally, larger-scale charges should be prepared to confirm performance and response to hazards stimuli.

A subsequent goal should be a research and development program to investigate the use of NTO in place of other more sensitive explosive ingredients in cast cured PBX's, which will provide the next generation of underwater explosives for use by the Australian Navy. Once again, issues of compatibility of NTO with cured and uncured binder systems must be addressed.

6. References

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Matthew W. Smith and Matthew D. Cliff

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19. ABSTRACT 3-Nitro-1,2,4-triazol-5-one (NTO) is an explosive ingredient under investigation as a potential insensitive replacement for RDX in explosive formulations. Although its performance is slightly less than that of RDX, NTO is thermally more stable and less sensitive to hazard stimuli. Explosive compositions based on NTO are therefore more likely to be Extremely Insensitive Detonating Substances, and munitions filled with them may meet the criteria of both Insensitive Munitions (IM) and HD 1.6 classification for storage and transportation. This report examines the currently available literature on NTO and its use in explosive compositions, and recommends future work to explore the possible application of NTO in IM compliant explosives for the ADF.					